United States Patent Application for:

MAINTENANCE OF PHOTORESIST ADHESION AND ACTIVITY ON THE SURFACE OF DIELECTRIC ARCS FOR 90 nm FEATURE SIZES

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1   [0001]   **MAINTENANCE OF PHOTORESIST ADHESION AND ACTIVITY ON**
2   **THE SURFACE OF DIELECTRIC ARCS FOR 90 nm FEATURE SIZES**

3   [0002]   **BACKGROUND OF THE INVENTION**

4   [0003]   1.   Field of the Invention

5   [0004]   The present invention relates to the fabrication of semiconductor devices

6   having feature sizes in the range of 90 nm and smaller. In particular, the invention relates

7   to a method of maintaining the adhesion of a photoresist to a surface during development

8   of a pattern in the photoresist and to maintenance of the functionality of a chemically

9   amplified photoresist on the surface of a dielectric anti-reflection coating (DARC).

10   [0005]   2.   Description of the Background Art

11   [0006]   As semiconductor devices are becoming ever smaller, the device features

12   necessarily become smaller. To produce feature sizes in the range of about 124 nm, for

13   example, a chemically amplified photoresist (CAR) is pattern imaged using a DUV

14   wavelength in the range of about 248 nm. To produce the next generation of feature

15   sizes, in the range of 90 nm, the CAR will be pattern imaged using a radiation wavelength

16   in the range of about 193 - 198 nm. The chemically amplified photoresists are typically

17   deposited over the surface of a DARC which reduces reflection during pattern radiation

18   imaging of the CAR. The composition of the DARC is determined by the refractive index

19   and extinction coefficient required to attenuate the radiation reflected off the surface of

20   the device substrate which underlies the DARC.

21   [0007]   The DARC used in combination with the CAR deep UV (DUV) photoresists

22   are frequently deposited by plasma enhanced chemical vapor deposition (PECVD). A

23   number of techniques have been described for deposition of PECVD films. In general,

24   the deposition techniques are closely tied to the apparatus used for the deposition,

25   although some parameters such as process chamber pressure, substrate temperature and

26   composition of the source gas used to provide the reactive species are relatively

1   independent of the apparatus peculiarities.

2   [0008]   In an article entitled "Dual Microwave -- R.F. Plasma Deposition Of

3   Functional Coatings" by J.E. Klemberg-Sapieha et al. in Thin Solid Films, 193/194

4   (1990) 965-972, the authors described the deposition of plasma silicon nitride (P-SiN)

5   and amorphous hydrogenated silicon (a-Si:H) films using a dual-frequency plasma. The

6   power source for the plasma consisted of a microwave discharge with RF power

7   simultaneously superimposed on the substrate holder. The negative substrate bias voltage

8   was said to substantially affect the deposition rate, the film composition, and the film

9   electrical properties. The authors report that ionic species are estimated to contribute

10   about 30 % to 40 % to the film growth rate. The increasing ion flux and energy with

11   increasing substrate bias voltage is said to enhance the formation of densely packed

12   coatings. As a result, the dielectric los tan δ of P-SiN, and the resistivity of a-Si:H is said

13   to be reduced by several orders of magnitude when the substrate bias voltage is raised

14   from 0 to -800V. The depositions were carried out in a large volume microwave plasma

15   (LMP®) apparatus of the kind available from AIXTRON AG and Fraunhofer IAF,

16   Freiburg, Germany, with a MW power at 2.45 GHz applied through a fused silica

17   window from a periodic slow wave structure. The substrate bias was applied at a

18   frequency of 13.56 MHz to a powered electrode which functioned as the substrate holder.

19   [0009]   A. Raveh et al. discuss the "Deposition and properties of diamond like carbon

20   films produced in microwave and radio-frequency plasma" in an article in J. Vac. Sci.

21   Technol. A 10(4), Jul/Aug 1992. In that article the authors report that hard a-C : H films

22   were grown in a dual frequency plasma sustained simultaneously by microwave and

23   radio-frequency power. Optimum growth conditions, namely those leading to the most

24   pronounced sp^3 structural features in the films, are said to depend very strongly on the

25   methane feed gas flow rate and on the argon concentration in the case of CH_4/Ar feed gas

26   mixtures. The optimum conditions are reported to be found to correspond to the

27   maximum values of ion flux at the growing film surface in combination with high

1   concentrations of precursor species such as CH, C2, C3, and atomic hydrogen in the

2   plasma, as revealed by optical emission spectroscopy. Films grown under optimum

3   conditions are said to have very high microhardness (~50 GPa), high density (1.8 g/cm^3),

4   and low internal stress (0.5 GPa). Addition of argon to the methane in the feed gas is

5   indicated as enhancing the gas phase fragmentation and raising microhardness, but argon

6   atoms trapped in the film structure increased internal stress. The apparatus which was

7   used to produce the films was the same apparatus as described above.

8   [0010]   International Application No. PCT/US00/20383, of Gill Yong Lee, published

9   February 8, 2001, discloses the use of a silicon-rich layer over the surface of a dielectric

10   ARC to prevent "resist poisoning". In particular, the DARC described is an inorganic

11   ARC layer such as silicon nitride (Si_xN_y) or silicon oxynitride (SiN_xO_y), or hydrogenated

12   silicon oxynitride. The DARC is said to be particularly useful during pattern imaging of

13   the photoresist, typically a CAR which relies on an acid formed in irradiated areas to

14   enable development of the pattern. However, the presence of amine radicles which are

15   contributed by the DARC contaminates the CAR applied over the DARC, neutralizing

16   the acid-generators. This makes the contaminated portions of the resist insoluble by the

17   developer. As a result, a "foot" is present at the base of the developed resist profile. To

18   prevent this problem, a capping layer is applied over the DARC prior to application of the

19   CAR. In one embodiment, the capping layer is silicon, preferably a thin amorphous

20   silicon layer. The silicon layer is said to be sufficiently thin to avoid causing standing

21   waves and interference in the resist. Alternatively, the cap layer may be a mono-atomic

22   layer that alters the surface morphology of the DARC. The mono-atomic layer, in one

23   embodiment comprises excess silicon dangling bonds on the surface of the DARC. For

24   example, the cap layer could comprise a silicon-rich oxide or a silicon-rich oxynitride if

25   the DARC comprised silicon oxide or an oxynitride layer.

26   [0011]   U.S. Patent No. 6,227,141 of Sharan et al., issued May 8, 2001, describes an

27   RF powered, plasma enhanced chemical vapor deposition reactor and methods of use of

1   the reactor. The plasma enhanced chemical vapor deposition (PECVD) apparatus makes

2   use of a first RF power source which delivers RF power at a first frequency to a first

3   electrode, and a second RF power source which delivers RF power at a second frequency

4   to a second electrode.

5   [0012]   Applied Materials, Inc., Santa Clara, California offers both single and dual

6   frequency PECVD chambers. The multifrequency processing chambers typically apply

7   two different RF power frequencies to a single electrode.

8   [0013]   U.S. Patent No. 6,171,764 to Ku et al., issued January 9, 2001 describes the

9   kinds of radiation reflection problems which may occur in photolithographic processes.

10   The description relates to semiconductor manufacturing processes which make use of a

11   dielectric anti-reflective (DARC) layer to reduce reflected radiation during photoresist

12   imaging. In particular, the difference between the Ku et al. invention and other known

13   methods is based on the ordering of specific layers in the substrate used in the

14   photolithographic process. In the Ku et al. method, the DARC layer is applied over a

15   substrate, followed by a hard mask layer, and then a photoresist. This is said to compare

16   with other known methods where the DARC layer is used between the photoresist layer

17   and the hard mask layer. (Col. 3, lines 35 - 46.)

18   [0014]   U.S. Patent No. 6,607,984 to Lee et al., issued August 19, 2003 describes a

19   method of semiconductor fabrication in which an inorganic anti-reflection coating is

20   employed and subsequently removed by selective etching relative to an underlying

21   inorganic dielectric layer. (Col. 1, lines 61 - 67, continuing at Col. 2 lines 1 - 6.)

22   [0015]   European Patent Application No. 99204265.5 of Shao -Wen Hsia et al.,

23   published June 21, 2000, describes a semiconductor interconnect structure employing an

24   inorganic dielectric layer produced by plasma enhanced chemical vapor deposition

25   (pecvd). In accordance with a preferred embodiment of the invention, a metal layer upon

26   which photoresist patterns are developed comprises a sandwiched metal stack having a

27   layer of conducting metal (aluminum, titanium, and the like) bounded by an upper thin-

1   film ARC layer and a bottom thin-film barrier layer, where at least the top layer is

2   composed of an inorganic dielectric substance. The use of an inorganic dielectric top

3   ARC layer is said to facilitate the use of thinner photoresist layers while preserving the

4   integrity of the photoresist pattern for deep sub-micron feature sizes. (Col. 1, lines 56 -

5   58, continuing at Col. 2, lines 1 - 8.)

6   [0016]   We have encountered a problem which does not appear to be addressed in the

7   known art, but which has become important in particular with respect to semiconductor

8   substrate features in the 90 nm range and smaller. During development of the

9   photoresist, applicants have encountered instances where the photoresist becomes

10 detached from the underlying substrate. Development refers to treatment of the

11 photoresist with a fluid, typically a liquid reagent, to remove portions of the photoresist,

12 thus creating a pattern. For reference purposes, when the portions of the photoresist

13 which are removed are the portions which have been exposed to patterning radiation, the

14 photoresist is said to be a positive photoresist. When the portions of the photoresist

15 which are removed are the portions which have not been exposed to patterning radiation,

16 the photoresist is said to be a negative photoresist.

17 [0017]   In addition to detachment of areas of the photoresist from the underlying

18 substrate, we have continued to observe reaction at the interface between an underlying

19 DARC and the photoresist. This reaction is despite the use of a nitrogen-free DARC. It

20 is possible to use a capping layer of the kind described in the art to isolate the photoresist

21 from an underlying DARC. However, typically the semiconductor manufacturing

22 process is a dual damascene process, which is common in multilevel metal devices. In a

23 dual damascene process, after the first photoresist patterning process, there is an etch

24 through underlying layers, including the DARC using the photoresist as a pattern.

25 Subsequently, the portions of the opened pattern are filled with a buried ARC (BARC),

26 followed by application of a second layer of photoresist and creation of a second pattern

27 in the photoresist. Typically the second layer of photoresist is in contact with the DARC

1   at the surface area where the etch passed through the DARC. Thus, there are still

2   significant photoresist "poisoning" problems even when a capping layer is applied over

3   the upper surface of the DARC as a part of the preparation for the first patterning step.

4   [0018]   A need exists for ensuring photoresist adhesion and uniform lithographic

5   imaging and development activity on the surface of various underlying substrates

6   (particularly on the surface of dielectric arcs) during the fabrication of semiconductor

7   devices with feature sizes of 90 nm and smaller.

8   [0019]   **SUMMARY OF THE INVENTION**

9   [0020]   We have traced the detachment of photoresist during development of patterned

10   features in the range of about 90 nm and smaller to a combination of the reduced "foot

11   print" of the pattern on the underlying substrate and to the contact angle between the

12   underlying substrate surface and the developing reagent used to develop a pattern in the

13   photoresist. We have determined that by maintaining a contact angle of about **20** degrees

14   or greater, and preferably 35 degrees or greater, the detachment of the photoresist from

15   the underlying substrate can be avoided for photoresists including feature sizes in the

16   range of about 90 nm. As feature sizes grow even smaller, it may be necessary to

17   continually increase the contact angle to maintain adhesion of the photoresist to the

18   underlying substrate during development of the photoresist. The key is to reduce the

19   force exerted against the photoresist wall as the feature size becomes smaller, with the

20   concurrent reduction in foot print of the photoresist on the underlying substrate surface.

21   [0021]   The contact or wetting angle of the substrate depends on the composition of

22   both the substrate and the developer used for photoresist development. The embodiments

23   described below pertain to a DARC, and in particular a DARC comprised of $SiO_xH_y : C$,

24   where x ranges from greater than 1 to about 2.0, and H ranges from about 0.1 to about

25   0.3, and the carbon content ranges from 0 % up to 5.0% (typically less than about 3.0%).

26   The reagents used to produce the DARC by PECVD are typically SiH_4, and CO_2, with

1   helium added as a diluent plasma source gas, which also provides species for surface

2   bombardment of the depositing film.   For a silane-based PECVD film deposition

3   process, where the silicon-containing precursor is SiH_4, the carbon content in the

4   polymeric film structure is typically less than about 3 %, which is contributed by CO_2

5   used in the firm formation process. We have discovered that an increase in carbon

6   content of the DARC produces a higher contact angle, which is beneficial in terms of

7   reducing the potential for detachment of the photoresist from the DARC surface during

8   development of the photoresist using a water based developer of the kind commonly used

9   in the semiconductor industry. To achieve a higher carbon content in the DARC, the

10   amount of CO_2 used in the SiH_4 /CO_2 process may be increased to some extent; in an

11   alternative, the silane-based precursor used in the PECVD deposition of the DARC may

12   contain carbon, such as trimethyl silane ($(CH_3)_3HSi$) or tetramethyl silane ($(CH_3)_4 Si$), for

13   example, but not by way of limitation.

14   [0022]   Other Group IV elements such as silicon, germanium, tin and lead, by way of

15   example and not by way of limitation, which are present in the DARC film may be

16   increased in concentration, in a manner similar to the carbon content, to increase the

17   contact angle between the DARC surface and the fluid photoresist developer.

18   [0023]   While an increased carbon content in the DARC increases the contact angle

19   and has a beneficial effect in terms of reducing photoresist detachment from the DARC

20   surface during development, a higher carbon content in a silane precursor for PECVD

21   film formation is generally more expensive and carbon particulate byproducts of the film

22   deposition may require more frequent deposition process chamber cleaning. The

23   improved attachment of the photoresist during development may justify the increased

24   chamber maintenance costs in terms of throughput in some instances. As an alternative,

25   it is possible to use a lower carbon content DARC, but to use a surface treatment of the

26   DARC to increase the contact angle with the developer; or to use a developer which

27   provides a higher contact angle on the DARC surface.

7

1   [0024]   We have achieved an increased contact angle between the DARC surface

2   and a water-based, basic CAR photoresist developer by treating the surface of the DARC

3   after formation of the DARC film. In particular, the DARC film surface has been treated

4   with a hydrogen plasma or a helium plasma to provide an increase in the contact angle.

5   Preferably, the hydrogen plasma is used for the DARC film surface treatment, as this

6   process provides a greater shelf life for the DARC coated substrate prior to subsequent

7   use and provides very good uniformity of performance across the entire substrate.

8   [0025]   The most commonly used DUV photoresists for semiconductor device

9   manufacture are the positive chemically amplified photoresists (CARs), which rely upon

10   the generation of an acid in the irradiated portion of the photoresist to form a latent image

11   which is subsequently developed using a basic developer. The photoresist pattern

12   developer is commonly a basic, water-based developer. The presence of a base on the

13   surface of a DARC at the time the CAR is applied causes subsequent problems in pattern

14   production, because the acid generated in the CAR upon irradiation reacts with the base

15   on the surface of the DARC, producing areas at the interface of the DARC and the CAR

16   which do not contain the acid generated by the irradiation. Development of the

17   photoresist pattern at this interfacial area does not occur properly when the basic

18   developing agent is applied to the photoresist. We have discovered that it is not enough

19   to remove nitrogen-containing species from the surface of the DARC. It is also necessary

20   to reduce the presence of OH groups from the surface of the DARC. The treatment of the

21   DARC surface with a hydrogen plasma prior to photoresist application to the DARC

22   surface not only increases the contact angle between the DARC and a water-based

23   photoresist developer, it also reduces the available OH groups on the surface of the

24   DARC, reducing photoresist poisoning during deposition, and pattern latent image

25   formation of the photoresist. Treatment of the DARC surface with helium prior to

26   photoresist application also tends to reduce the available OH groups on the surface of the

27   DARC, but has a limited performance time window, and has been less uniform in ability

1   to reduce photoresist poisoning under currently known treatment conditions.

2   [0026]   **BRIEF DESCRIPTION OF THE DRAWINGS**

3   [0027]   Figure 1 A shows a diagram 100 of a liquid droplet 102 in contact with a

4   substrate 103, where the contact angle 104, referred to as α_1, in the range of about 18

5   degrees.

6   [0028]   Figure 1B shows a diagram 100 of a liquid droplet 106 in contact with a

7   substrate 103, where the contact angle 108, referred to as α_2, is in an acceptable range,

8   about 70 degrees, for the present invention.

9

10   [0029]   Figure 1C shows a diagram 100 of a liquid droplet 110 in contact with a

11   substrate 103, where the contact angle 112, referred to as α_3, is in an acceptable range,

12   about 155 degrees, for the present invention

13   [0030]   Figure 2A shows a schematic top view 200 of an SEM image for a developed

14   CAR on the surface of a $SiO_x N_y$ DARC , where the contact angle between the DARC and

15   the developer for the photoresist was about 5.1 degrees.

16   [0031]   Figure 2B shows a schematic top view 210 of an SEM image for a developed

17   CAR on the surface of a $SiO_x H_y$ DARC, where the contact angle between the DARC and

18   the developer for the photoresist was about 3.7 degrees.

19   [0032]   Figure 2C shows a schematic top view 220 of an SEM image for a developed

20   CAR on the surface of a $SiO_x H_y$ DARC, where the contact angle between the DARC and

21   the developer for the photoresist was about 34.5 degrees.

1   [0033]   Figure 2D shows a schematic top view 230 of an SEM image for a developed

2   CAR on the surface of a hydrogen plasma treated SiO_xH_y DARC, where the contact angle

3   between the DARC and the developer for the photoresist was about 63 degrees.

4   [0034]   Figure 2E shows a schematic top view 240 of an SEM image for a developed

5   CAR on the surface of a silicon-rich, nitrogen- free DARC, where the contact angle

6   between the DARC and the developer for the photoresist was about 3.5 degrees.

7   [0035]   Figure 3 is a graph showing the change in contact angle between a nitrogen-

8   free DARC 193 , SiO_xHy surface and a water-based alkaline photoresist developer, where

9   the DARC 193 surface was treated with a helium plasma. Initially, the contact angle

10   between the DARC surface and the developer was about 30 degrees to about 40 degrees

11   depending on the plasma treatment time. The contact angle change is shows as a function

12   of passing time in days, where each curve represents a different helium plasma treatment

13   period.

14   [0036]   Figure 4 is a graph showing the change in contact angle between a nitrogen-

15   free DARC 193, SiO_xHy surface and HMDS photoresist developer, where the DARC 193

16   surface was treated with a hydrogen plasma. Initially, the contact angle between the

17   DARC surface and the developer was about 60 degrees. The contact angle change is

18   shows as a function of passing time in days, where each curve represents a different

19   hydrogen plasma treatment period.

20   [0037]   Figure 5 is a graph 500 showing the compressive stress on scale 504 of a

21   nitrogen-free DARC 193 film of varying atomic composition, as a function of the process

22   conditions on scale 502, where single frequency (SF) plasma deposition was used in some

23   instances and multiple frequency (MF) plasma deposition was used in other instances. In

1   addition, in some instances the inert gas in the plasma source gas was argon (AR), while

2   in some other instances the inert gas was helium (He).

3   [0038]   Figure 6 is a graph 600 showing reduction in extinction coefficient, k, after

4   O_2 ashing for photoresist removal, on scale 604, of a nitrogen-free DARC 193 film, where

5   films of varying nitrogen composition were evaluated, as a function of the process

6   conditions on scale 602, where single frequency (SF) plasma deposition was used in some

7   instances and multiple frequency (MF) plasma deposition was used in other instances. In

8   addition, in some instances the inert gas in the plasma source gas was argon (AR), while

9   in some other instances the inert gas was helium (He).

10   [0039]   Figure 7 is a graph 700 showing change in extinction coefficient, k, after 9

11   days of storage at room temperature in ambient atmosphere of a clean room, on scale 704,

12   of a nitrogen-free DARC 193 film, where films of varying nitrogen composition were

13   evaluated, as a function of the process conditions on scale 702, where single frequency

14   (SF) plasma deposition was used in some instances and multiple frequency (MF) plasma

15   deposition was used in other instances. In addition, in some instances the inert gas in the

16   plasma source gas was argon (AR), while in some other instances the inert gas was

17   helium (He).

18   [0040]   Figure 8 is a graph 800 showing the post oxygen plasma ashing reduction in

19   refractive index (n) on scale 802, for a nitrogen-free DARC 193 film, as a function of the

20   compressive stress of the DARC film on scale 804. Curve 806 represents a DARC film

21   having an extinction coefficient (k) of 0.35; Curve 808 represents a DARC film having a

22   k of 0.6; and Curve 810 represents a DARC film having a k of 0.95. The extinction

23   coefficient is a function of the chemical composition of the film. The thickness of each

24   film was about 250 Å.

1

2   [0041]   Figure 9 is a graph 900 showing the post oxygen ashing reduction in

3   extinction coefficient (k) on scale 902, for a nitrogen-free DARC 193 film, as a function

4   of the compressive stress of the DARC film on scale 904. Curve 906 represents a DARC

5   film having an initial extinction coefficient (k) of 0.35; Curve 908 represents a DARC

6   film having an initial k of 0.6; and Curve 910 represents a DARC film having an initial k

7   of 0.95. The thickness of each film was about 250 Å.

8   [0042]   **DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS**

9   [0043]   As a preface to the detailed description, it should be noted that, as used in this

10   specification and the appended claims, the singular forms "a", "an", and "the" include

11   plural referents, unless the context clearly dictates otherwise.

12   [0044]   As mentioned above, we have traced the detachment of photoresist during

13   development of patterned features in the range of about 90 nm and smaller to a

14   combination of the reduced "foot print" of the pattern on the underlying substrate and to

15   the contact angle between the underlying substrate surface and the developing reagent.

16   We have determined that by maintaining a contact angle of about 20 degrees or greater,

17   preferably 35 degrees or greater, the detachment of the photoresist from the underlying

18   substrate can be avoided for photoresists including feature sizes in the range of about 90

19   nm or smaller.

20   [0045]   Figure 1A is a simple diagram showing a top view of a substrate surface 103

21   with a liquid droplet 102 on the surface 103. The contact angle between the surface 103

22   and droplet 102 is the angle between the horizontal substrate surface and a tangent drawn

23   along the curvature of the droplet 102 at the edge of droplet 102. The contact angle can

24   approach zero degrees when the droplet 102 wets surface 103 well and the tangent line is

25   nearly flat. In Figure 1A, the contact angle 102, referenced as α_1, is illustrated as being

26   about 18 degrees. This contact angle is just slightly below the minimum contact angle we

1   have determined to be adequate to protect a photoresist having 90 nm feature sizes against

2   detachment from an underlying surface during development of a latent irradiated image in

3   the photoresist (into a patterning mask having the 90 nm features).

4   [0046]   Figure 1B shows another droplet 106 of a material which forms a contact

5   angle 108, referenced as α_2, with substrate 103. The contact angle in Figure 1B is

6   illustrated as being about 70 degrees, well above the minimum contact angle of about 20

7   degrees which is recommended to prevent photoresist detachment for 90 nm photoresist

8   features.

9   [0047]   The basic concept of the present invention with respect to the affect of contact

10   angle on adhesion of photoresist to an underlying substrate during development of the

11   photoresist is applicable to any underlying substrate and the developing fluid used to

12   develop the photoresist. For purposes of illustration, the experimental embodiments

13   described were carried out using DARC® (Applied Materials, Inc.) 193 substrates. In

14   some instances, the surfaces of the DARC® 193 substrate was surface treated prior to

15   application of the photoresist. The initial adhesion studies were carried out on DARC®

16   193 substrates where the photoresist applied over the substrate and developed into a

17   pattern was a developer used during the initial adhesion study was a SHIPLEY® UV6

18   (248 nm) CAR. The developer used to develop the UV6 CAR was a

19   tetramethylammonium hydroxide (TMAH)-containing aqueous alkaline solution, with the

20   specific formulation being that recommended by Shipley Company, Marlborough,

21   Massachusetts, for developing the Shipley UV6 CAR. Subsequent to the initial studies,

22   additional experimentation has been carried out in which a JSR AT237 CAR (193 nm)

23   photoresist was used for purposes of evaluating the effect of photoresist adhesion and

24   poisoning effects with respect to 90 nm pattern feature sizes.

25   [0048]   The initial adhesion studies, which used the SHIPLEY® UV 6 photoresist

26   employed a photoresist thickness in the range of about 3,000 Å to about 4,000 Å. The

13

1   patterning of the photoresist was carried out using a CANON® FPA-5000ES2 exposure

2   tool which provided 248 nm radiation. The target feature was a 100nm line/120nm space.

3   The reticle was a SCAA mask. An HMDS treatment was carried out on the DARC

4   substrate for 30 seconds prior to photoresist application. The development of the

5   photoresist was carried out for 60 seconds under conditions recommended for the

6   SHIPLEY® UV6 photoresist.

7   [0049]   A typical experimental substrate included, from bottom to top, a silicon

8   substrate; a 600 Å thick layer of α-carbon; a 250 Å thick layer of DARC or DARC 193; a

9   treated surface on the DARC or DARC 193, or a capping layer over the DARC or DARC

10   193 surface; and an approximately 3,200 Å thick layer of the Shipley UV 6 CAR.

11   [0050]   The DARC and DARC 193 anti-reflective coatings which were used in the

12   experimental embodiments were applied using PECVD in an Applied Materials, Inc.

13   PRODUCER® system in a twin PECVD processing chamber. Applied Materials, Inc.

14   has offices in Santa Clara, California. The comparative example DARC film was a

15   standard SiO_xN_y, where x was approximately 1.25 and y was approximately 0.25.

16   [0051]   The DARC 193 was a nitrogen-free SiO_xH_y :C film, where x ranged from

17   greater than 1 to about 2.0, and y ranged from about 0.1 to about 0.3, with a carbon

18   content ranging from about 0 % to 5 %, and typically in the range of about 3 %, unless

19   specified to be different. The precursors used to produce the DARC 193 film were silane

20   (SiH_4), CO_2, and helium. An additional nitrogen-free DARC 193 film was made to

21   achieve increased carbon content in the film, where the precursor silane was trimethyl

22   silane $(CH_3)_3HSi$. However, one skilled in the art will understand that other carbon-

23   containing silanes could be substituted as precursor materials for deposition of the DARC

24   by PECVD techniques known in the art.

25   [0052]   As previously mentioned, although an increased carbon content in the DARC

26   increases the contact angle and has a beneficial effect in terms of reducing photoresist

1　　detachment from the DARC or DARC 193 surface during development, the higher carbon

2　　content silane precursors for PECVD film formation are more expensive and require more

3　　frequent process chamber cleaning. The improved attachment of the photoresist during

4　　development may justify the increased chamber maintenance costs in terms of throughput

5　　in some instances. Other Group IV elements such as (an increased amount of) silicon, or

6　　germanium, or tin, or lead, for example and not by way of limitation, may be incorporated

7　　into a DARC or DARC 193 film to increase the contact angle. One skilled in the art can

8　　determine with minimal experimentation the amount of the Group IV element which must

9　　be included to obtain a contact angle which is adequate, in view of the present disclosure.

10　　[0053]　　　As an alternative to inclusion of a Group IV element other than silicon, or to

11　　increasing the silicon content in the DARC or DARC 193 film, it is possible to use a

12　　surface treatment of the DARC to reduce the contact angle with the developer; or to use a

13　　developer which provides a higher contact angle on the DARC surface.

14　　[0054]　　　We have achieved an increased contact angle between the DARC surface and

15　　a water-based, alkaline CAR photoresist developer by treating the surface of the DARC

16　　after formation of the DARC. We have demonstrated that treatment of a DARC film after

17　　formation with a hydrogen plasma or a helium plasma increases the contact angle between

18　　the DARC surface and a water-based photoresist developing agent. The hydrogen and

19　　helium plasma treatments of a deposited DARC film were carried out in a PRODUCER®

20　　twin PECVD chamber using a single frequency RF power source for plasma generation.

21　　Preferably, the hydrogen plasma is used for the DARC film surface treatment, as this has

22　　provided a long shelf life for the DARC coated substrate prior to application of a

23　　photoresist and has provided better uniformity of performance across a wafer substrate

24　　compared with a helium treatment, as will be discussed in more detail below.

25　　[0055]　　　The DARC 193 film typically used in the example embodiments described

26　　below was deposited in the PRODUCER® twin PECVD chamber of Applied Materials,

1   Inc.

2   [0056]   In some instances, the DARC 193 film was prepared using a single 13.56

3   frequency RF power source. The general process conditions for a $SiO_xH_y:C$ 193 DARC

4   film deposition using a single frequency power source were: SiH_4 flow rate of 40 to 80

5   sccm, CO_2 flow rate of 900 to 4,000 sccm, He flow rate of 2,000 sccm to 12,000 sccm;

6   plasma source power 100 W to 175W; spacing between the shower head and the substrate

7   ranged from 400 mils to 800 mils; the substrate temperature was 350 °C ± 50 °C; the

8   process chamber pressure ranged between 4 Torr and 8 Torr.

9   [0057]   In other instances, a multiple frequency, typically a dual frequency RF power

10   source was used to generate the plasma, where each of the multiple frequency power

11   applications was made to the same electrode. Table I, below, shows a series of process

12   conditions and measured values representative of production of the $SiO_xH_y:C$ films in

13   the PRODUCER® twin PECVD process chamber. The application of dual frequency

14   power sources during deposition of the DARC 193 $SiO_xH_y:C$ films has proved to reduce

15   photoresist poisoning, increase the shelf life of the DARC 193 coated substrate prior to

16   photoresist application, and has improved maintenance of refractive index and extinction

17   coefficient of the DARC 193 film during oxygen plasma ashing for removal of residual

18   photoresist, as will be discussed in more detail subsequently herein.

[0058]   TABLE I

MULTIPLE FREQUENCY DARC 193 FILM DEPOSITION PROCESS AND DATA

SiH_4 (sccm)	CO_2 (slm)	He (slm)	Pressure (Torr)	HF (Watts)	LF (Watts)	Thic k-ness (Å)	n (193nm)	k @ 150Å	k @ 250Å	Stress (Mpa)
40	2.5	5	5.5	65	20	152	1.8098	0.2292	0.2914	-163
40	2.5	5	5.5	65	20	151	1.8084	0.2281	0.2960	
40	1.8	6	5.5	65	15	156	1.7736	0.2958	0.3686	-154
40	1.8	6	5.5	65	15	156	1.7762	0.2943	0.3718	
40	2.5	6	5.5	65	20	149	1.8216	0.1992	0.2720	-172
40	2.5	6	5.5	65	20	148	1.8082	0.2101	0.2813	
40	2.5	6	4.8	65	15	147	1.8103	0.2015	0.2762	-156
40	2.5	6	4.8	65	15	146	1.7849	0.2169	0.2777	
40	3.0	6	5.5	65	20	148	1.8065	0.1846		
40	3.5	6	5.5	65	20	141	1.8433	0.1297		
40	4.0	6	5.5	65	20	140	1.8061	0.1132		

[0059]   The substrate temperature for all of the film preparation was 350 ± 50°C. The HF (high frequency) power was at 13.56 MHz; the LF (low frequency) power was at 350 kHz. The spacing between the shower head and the substrate was approximately 500 mils. The film deposition time was 8.5 seconds; and the deposition rate ranged from about 990 to about 1075 Å per minute. The symbol "n" represents refractive index, and the symbol "k" represents the extinction coefficient. Sccm refers to standard cc per minute; slm refers to standard liters per minute. The reference to 150 Å and 250 Å with respect to the k value indicates the thickness of the DARC.193.

[0060]   The nitrogen-free (N-free) dielectric anti-reflective coating SiO_xH_y :C was

developed to reduce the poisoning interaction caused when NO_2 is used as a precursor

during deposition of the DARC 193. However, we learned, after considerable testing,

that the presence of -OH radicals, which either exist inherently in the DARC or result

from H_2O absorption on the DARC surface also cause photoresist poisoning of a CAR

1 positive photoresist. Current investigation has revealed that poisoning can be eliminated

2 by surface acidification of the DARC after deposition. The DARC surface acidification

3 circumvents the neutralization of photo-generated H+ in the CAR by the -OH radicals

4 inherently in the DARC. In addition, we have discovered that a more dense ARC film

5 makes it difficult for -OH radicals to form on the DARC surface due to H_2O absorption.

6 Compressive film stress is an indication of film density, and directly correlates to

7 resistance to H_2O absorption on the DARC film surface.

8 [0061]   It was possible to greatly improve the DARC resistance to H_2O absorption by

9 creating and maintaining a deposition process regime that makes the DARC film more

10 dense. This dense DARC film with an acidified surface has demonstrated promising

11 lithography performance with minimal resist poisoning, as well as excellent shelf life and

12 O_2 ashing resistance. Combination of DARC film densification, DARC film surface

13 acidification, and a DARC film surface which provides a high contact angle during

14 development of the photoresist ensures both excellent pattern development and adhesion

15 of the photoresist during development for 193 nm lithography, and during the patterning

16 of 90 nm and smaller features.

17 [0062]   For reference purposes, a PECVD nitrogen-containing DARC typically has a

18 composition $SiO_xN_y{:}H$, where Si is typically about 55 atomic percent, O is about 35

19 atomic percent and N is about 15 % or less of the DARC composition. The new N-free

20 DARC 193 composition $SiO_xH_y : C$ is such that Si ranges from about 40 atomic % to 45

21 atomic %, O ranges from about 40 atomic % to 51 atomic %, H ranges from about 4

22 atomic % to about 15 atomic %, and C ranges from about 0 atomic % to about atomic

23 5%, but is typically less than about 3 atomic %. The DARC 193 is produced by PECVD

24 using SiH_4, an oxygen source, and an inert gas as precursors. When the oxygen source is

25 CO_2, this contributes carbon to the DARC 193 film.

26 [0063]   When the silane used as a precursor contains carbon, such as a trimethyl or

27 tetramethyl silane, for example, the DARC 193 film contains Si ranging from about 20

1   atomic % to 50 atomic %, O ranges from about 10 atomic % to about 20 atomic %, H

2   ranges from about 10 atomic % to about 50 atomic %, and C ranges from about 10 atomic

3   % to about 50 atomic %.

4   [0064]   When photoresist poisoning occurs, electron pairs from a basic group attract

5   protons from the 193 nm positive-acting chemically-amplified photoresist, neutralizing

6   the formation of an acid in irradiated areas of the photoresist, typically at the interface of

7   the photoresist adjacent the DARC surface. The poisoning manifests itself as a bump in

8   via structures, footing, scums, and a rough surface on a substrate.

9   [0065]   We determined that use of multiple frequency power application during

10   deposition of a DARC increases the density of the DARC film, as previously mentioned;

11   this improves the film resistance to H_2O absorption. As a result, the shelf life of the

12   deposited DARC film and the maintenance of refractive index and extinction coefficient

13   of the DARC film is improved with the use of multiple, typically dual, frequency power

14   application during the deposition of the DARC film. By using optical measurements and

15   FTIR, we were able to correlate film stress, which is an indicator of film density, with the

16   increased shelf life and maintenance of refractive index and extinction coefficient for a

17   variety of different film compositions. The detailed data is presented in the embodiment

18   examples provided below.

19   [0066]   However, the DARC films deposited under process conditions which

20   produce a dense film, such as a plasma source gas flow rate of SiH_4 at 40 sccm, CO_2 at

21   2.5 slm, and He at 6 slm; at a pressure of 5.5 Torr, with 65 W of HF power and 20 W of

22   LF power, for example, and not by way of limitation, exhibit a contact angle in the range

23   of about 5 degrees. Although the photoresist poisoning problem may be avoided by the

24   dense film, when the patterned feature size of the photoresist is 120 nm or smaller, and

25   particularly 90 nm and smaller, this contact angle is not adequate to ensure that the

26   photoresist will remain attached to the DARC film surface during development of the

27   photoresist pattern.

1   [0067]   As discussed above, when the composition of a DARC 193 (SiO_xH_y : C) film

2   does not provide an adequate contact angle, or when the developed pattern is poor, it is

3   possible to increase the contact angle and to reduce resist poisoning by treating the

4   surface of the DARC 193 film after deposition. We have treated various DARC 193 film

5   surfaces with plasmas of CO_2, H_2, and He. We have also placed a capping layer of α-

6   silicon on the DARC 193 film surface. The results achieved using these surface

7   treatment techniques are illustrated in Figures 2A through 2E. The DARC 193 films

8   which were treated were prepared using dual frequency RF power application of the kind

9   described above.

10   [0068]   EXAMPLE EMBODIMENTS

11   [0069]   Example One:

12   [0070]   As a comparative example, a SiON DARC having an n (refractive index) of

13   1.9 and a k (extinction coefficient)of 0.3 @ 248 nm was capped with a 50 Å thick silicon

14   oxide capping film generated from a SiH_4 /CO_2/ helium plasma using the general PECVD

15   conditions of the kind described above for a single frequency plasma deposition process.

16   The capped DARC exhibited a contact angle of 5.1 degrees with the water based alkaline

17   developer used to develop the CAR, which was the SHIPLEY® UV6 photoresist. After

18   exposure to either 230 J or 280 J of 248 nm patterning radiation, followed by

19   development of the pattern, a photomicrograph of a top view 200 of the developed

20   photoresist had the appearance illustrated by the schematic shown in Figure 2A. The

21   oxide-capped SiON DARC surface 202 was completely exposed in patterned areas after

22   development of the photoresist, because the lines and spaces pattern which was to be

23   developed failed due to detachment of the photoresist during development in areas 204.

24   [0071]   Example Two:

25   [0072]   As a second comparative example, a nitrogen-free DARC 193 SiO_xH_y : C

26   film having an n of 1.9 and a k of 0.3 @ 248 nm, which was surface treated with a CO_2

27   plasma for a time period of about 20 seconds, using a CO_2 flow rate of about 3slm in a 200

1   mm PRODUCER® twin PECVD process chamber, using the single frequency plasma

2   deposition process. The pressure was about 5 Torr, at a substrate temperature of about

3   350 °C, at a plasma source power of about 50 - 100 W at 13.56 MHz, and at a shower head

4   spacing of 450 mils from the substrate surface. The CO_2-treated DARC 193, exhibited a

5   contact angle of only 3.5 degrees with respect to the photoresist water-based alkaline

6   developer. Exposure of the CAR to either 230 J or 280 J of 248 nm patterning radiation,

7   and development of the imaged photoresist resulted in a developed photoresist where none

8   of the patterned areas were present. All of the developed feature areas became detached

9   from the DARC surface and washed away on development.

10   [0073]   Example Three:

11   [0074]   As a third comparative example, a nitrogen-free DARC 193 SiO_xH_y : C film

12   having an n of 1.9 and a k of 0.3 @ 248 nm, which was not surface treated, exhibited a

13   contact angle of about 3.7 degrees with respect to the same developer mentioned with

14   respect to Example Two. Exposure of the SHIPLEY® UV6 photoresist to 230 J of 248

15   nm patterning radiation, followed by development of the latent irradiated image in the

16   photoresist, produced a relatively acceptable pattern. However, exposure of the CAR to

17   280 J of 248 nm patterning radiation, followed by development, produced a defective

18   pattern in the CAR of the kind illustrated in Figure 2B. Figure 2B is a schematic top view

19   210 of a photomicrograph of the patterned photoresist. The DARC 193 surface 212 was

20   exposed in some areas where the photoresist 216 should have been present. The

21   photoresist 216 became detached, leaving broken off areas 214 where photoresist was

22   missing. The difference in the developed pattern with such a slight difference in the

23   amount of energy applied during radiation of the pattern indicates that the combination of

24   the imaging and development process is not reliable for manufacturing purposes. We

25   needed to provide an imaging and development process which was sufficiently reliable for

26   production.

27   [0075]   Example Four:

1   [0076]   In a first example of the invention, a DARC 193 SiO_xH_y : C film having an n

2   of 1.9 and a k of 0.3 @ 248 nm, which was surface treated with a single frequency-

3   generated hydrogen plasma for a time period of about 10 seconds, using a hydrogen flow

4   rate of 600 sccm in the 200 mm PRODUCER® twin PECVD process chamber, at a

5   pressure of ranging from about 2 Torr to about 10 Torr (typically about 5.5 Torr), at a

6   substrate temperature of about 350 ±50 °C, at a plasma source power of 300W at 13.56

7   MHz, and at a shower head spacing of 450 mils from the substrate surface, exhibited a

8   contact angle of about 63 degrees with respect to the same developer mentioned with

9   respect to Example Three. Exposure of the photoresist to either 230 J/m^2 or 280 J/m^2 of

10   248 nm patterning radiation, followed by development of the image using the developer

11   produced a very acceptable pattern of approximately 110 nm features in the CAR. The

12   pattern produced is illustrated in Figure 2D. Figure 2D is a top view 230 of a

13   photomicrograph of the patterned photoresist. Experimentation has indicated that the

14   nitrogen-free DARC 193 with the hydrogen surface treatment has a comparable

15   lithography window with respect to a BARC used for poly gate applications. This is

16   because the H_2 treatment does not affect reflectivity as much as a capping layer of α-

17   silicon, for example.

18   [0077]   Example Five:

19   [0078]   In a second example of the invention, a DARC 193 SiO_xH_y : C film having an

20   n of 1.9 and a k of 0.3 @ 248 nm, which was surface treated with a helium plasma

21   generated using a single frequency power source, for a time period of about 10 to about 30

22   seconds, using a helium flow rate of 5 slm in the 200 mm PRODUCER® twin PECVD

23   process chamber, at a pressure of ranging from about 2 Torr to about 10 Torr (typically

24   about 5.5 Torr), at a substrate temperature of about 350 ±50 °C, at a plasma source power

25   of 50 - 100 W at 13.56 MHz, and at a shower head spacing of 450 mils from the substrate

26   surface, exhibited a contact angle of about 32 degrees to about 40 degrees (for the 10

27   second and 30 second treatment periods, respectively) with respect to the same developer

1   mentioned above. Exposure of the photoresist CAR to 230 J/m^2 or 280 J/m^2 of 248 nm

2   patterning radiation, followed by development of the image using the developer produced

3   an acceptable pattern of approximately 110 nm features in the CAR over the substrate

4   surface as a whole. However, there were some areas on the substrate surface which were

5   substandard. There is no representative Figure shown which illustrates this example.

6   [0079]   Example Six:

7   [0080]   In a third example of the invention, a nitrogen-free DARC 193 SiO_xH_y : C film

8   having an n of 1.9 and a k of 0.3 @ 248 nm, which was capped with a 15 Å thick α-Si

9   coating applied by discontinuing the CO_2 reagent feed to the DARC 193 single frequency

10 plasma deposition process. The α-silicon deposition time period was about 5 seconds,

11 using a SiH_4 flow rate of 10 sccm and helium at a 6 slm flow rate in the 200 mm

12 PRODUCER® twin PECVD process chamber, at a pressure of ranging from about 2 Torr

13 to about 10 Torr (typically about 5.5 Torr), at a substrate temperature of about 350 ±50 °C,

14 at a plasma source power of 50 W at 13.56 MHz, and at a shower head spacing of 500 mils

15 from the substrate surface, exhibited a contact angle of about 34.5 degrees with respect to

16 the water-based, basic developer. Exposure of the CAR to either 230 J/m^2 or 280 J/m^2 of

17 193 nm patterning radiation, followed by development of the image, produced a very

18 acceptable pattern of 90 nm features in the CAR which is illustrated in Figure 2C. Figure

19 2C is a schematic top view 230 of a photomicrograph of the patterned photoresist. The

20 DARC 193 surface 232 was properly exposed in the developed areas, leaving the

21 photoresist 236 present in desired areas of the approximately 110 nm feature size pattern.

22 Although this example is for an α-silicon capping film, an α-carbon capping film is

23 expected to provide similar results.

24 [0081]   Example Seven

25 [0082]   Figure 2E illustrates a schematic top view 240 of a nitrogen-free DARC 193

26 SiO_xH_y : C film having an n of 1.9 and a k of 0.8 @ 248 nm. The increased k was

27 obtained by reducing the carbon content of the film to less than about 2.0 %, and

1   increasing the S-H content of the film during deposition of the film, using the process

2   parameters described above with respect to a nitrogen-free DARC 193 deposition.

3   However, the increase in S-H content of the film was inadequate and did not produce a

4   contact angle which was helpful. The contact angle obtained was 3.5 degrees, and

5   photoresist detachment was observed during development of the photoresist. Although a

6   230 J/m^2 exposure during patterning did produce an acceptable, the 280 J/m^2 exposure did

7   not. The schematic top view 240 of the developed pattern for the 280 J/m^2 exposure,

8   which is illustrated in Figure 2E, shows that, due to detachment and shifting of the

9   location of portions of the photoresist 246 during development, the DARC 193 surface

10   242 did not exhibit the proper pattern.

11   [0083]   Figure 3 is a graph 300 illustrating the shelf life of the contact angle for a

12   DARC 193 film which is contacted with an aqueous, basic developer, where the DARC

13   193 film surface was treated with a helium plasma to improve the contact angle. After

14   deposition of the nitrogen-free DARC 193 $SiO_xH_y : C$ film, the substrate was stored in air

15   at room temperature (about 27 °C) under typical clean room conditions. The contact angle

16   is shown on scale 310, with the days after DARC 193 formation and helium plasma

17   treatment shown on scale 308. Curve 302 illustrates the change in contact angle for a

18   DARC 193 film, n $\cong$ 1.9, k $\cong$ 0.3 @ 248 nm (a low k DARC), which was exposed to 10

19   seconds of helium plasma treatment. Curve 304 illustrates the change in contact angle for

20   the DARC 193 film which was exposed to 30 seconds of helium plasma treatment. Curve

21   306 illustrates the change in contact angle for the DARC 193 film which was exposed to

22   60 seconds of helium plasma treatment. It is a surprising result that the longer treatment

23   times caused the change in contact angle to be more rapid and that the change resulting

24   from longer treatment times could be so drastic as to cause the contact angle to fall to

1   about 28 degrees. For example, when the helium plasma treatment time is 60 seconds, the

2   contact angle drops below 30 degrees within 3 days, while the 10 second treatment

3   provided a 35 degree contact angle after 6 days.

4   [0084]   Figure 4 is a graph 400 illustrating the shelf life of the contact angle for a DARC

5   193 film, n ≅ 1.9, k ≅ 0.3 @ 248 nm (a low k DARC), which is contacted with the aqueous,

6   basic developer, where the DARC 193 film surface was treated with a hydrogen plasma

7   and then stored in the manner described with reference to Figure 3. The contact angle is

8   shown on scale 410, with the days after DARC 193 formation and hydrogen plasma

9   treatment shown on scale 408. Curve 402 illustrates the change in contact angle for the

10   DARC 193 film which was exposed to 10 seconds of hydrogen plasma treatment. Curve

11   404 illustrates the change in contact angle for the DARC 193 film which was exposed to

12   30 seconds of hydrogen plasma treatment. Curve 406 illustrates the change in contact

13   angle for the DARC 193 film which was exposed to 60 seconds of hydrogen plasma

14   treatment. In the instance of a hydrogen plasma treatment, the change in contact angle is

15   relatively small over a six day time period, with a slight increase in the contact angle

16   toward the end of the six day time period. This may be indicative of a reaction taking

17   place between the surface of the DARC 193 film and the hydrogen so that the hydrogen

18   becomes a permanent part of the DARC 192 film surface. This is in contrast with the

19   DARC 193 film treated with the helium plasma, where helium may be absorbed on the

20   film surface rather than reacted with the surface, since the surface shows a significant

21   decrease in contact angle over a time period.

22   [0085]   The indication that the helium plasma treatment alters the contact angle of the

1   DARC 193 surface in a temporary manner does not mean that the helium plasma treatment

2   is not useful; it simply means that the DARC 193 surface must be used within a relatively

3   short time period.

4   [0086]   The other concern in the production of feature sizes of 120 nm or less, and in

5   particular 90 nm or less, is that there will be photoresist poisoning even though the

6   photoresist remains attached during development. To have proper pattern formation, it is

7   necessary that the photoresist remain attached to the substrate during development and that

8   photoresist poisoning, which will prevent proper pattern development, be avoided. At the

9   time of development of the nitrogen-free DARC 193, it was anticipated that the absence of

10   nitrogen would eliminate the poisoning of the acid-based positive CAR, as previously

11   discussed. However, it was discovered that the presence of -OH radicals on the surface of

12   the DARC 193 continued to create photoresist poisoning problems. -OH radicals were

13   suspected to be present due to moisture absorption of the DARC 193 surface.

14   [0087]   To avoid photoresist poisoning when the nitrogen-free DARC 193 SiO_xH_y :

15   C film is used, we tried two different approaches. The first approach was to density the

16   surface of the film so that H_2O absorption would not occur on the film surface. The

17   second approach was to acidify the film surface to neutralize the effect of H_2O absorption.

18   [0088]   We evaluated the differences in reaction with O_2 plasma and in H_2O

19   absorption on the surfaces of nitrogen-free DARC 193 SiO_xH_y : C films of differing

20   atomic composition, where the films were produced using the single frequency and dual

21   frequency PECVD deposition techniques described above. The atomic compositions of

22   the films were adjusted so that k = 0.35, or k = 0.6, or k = 0.95, with k values being ± 0.05.

23   We also evaluated the effect of using helium as the inert gas in the plasma source gas

1   compared with argon as the inert gas.

2   [0089]   The photoresist applied over the nitrogen-free DARC 193 film was TARF-

3   6A-101, available from TOK company (Tokyo Ohka Kogyo Co. ltd.) of Kawasaki, Japan,

4   a 193 nm radiation exposure CAR. The patterning of this film was carried out using a

5   CANON® AS 2 radiation source. The pattern was developed using an aqueous, basic

6   developer supplied by TOK company for use with the TARF-6A-101 photoresist.

7   [0090]   Figure 5 is a graph showing compressive stress in Mpa on scale 504, for a

8   nitrogen-free DARC 193 SiO_xH_y : C film of varying atomic composition (which provides

9   a k = 0.35, k = 0.6, or k = 0.95, as a function of process conditions indicated on the 502

10   scale. SF represents a single frequency PECVD deposition of the DARC 193 film, while

11   MF indicates a multiple (dual) frequency PECVD deposition of the DARC 193 film. Ar

12   represents the use of argon as the inert gas in the plasma source gas, while He indicates

13   helium as the inert gas in the plasma source gas. The compressive stress for each film

14   composition is shown to increase when MF frequency deposition is used and when helium

15   is used as the inert gas. In addition, when the power input to the plasma is reduced, so that

16   the film is deposited more slowly, it is possible to get a significant increase in compressive

17   stress of the film. Curve 506 represents a nitrogen-free DARC 193 film having an initial

18   extinction coefficient of 0.35; Curve 508 represents the DARC 193 film having an initial

19   extinction coefficient of 0.6; and Curve 510 represents the DARC 193 film having an

20   initial extinction coefficient of 0.95. A higher compressive stress of the film has been

21   correlated to a more dense film, as described below.

22   [0091]   Figure 6 is a graph 600 which shows the reduction in extinction coefficient on

23   scale 604 for the nitrogen-free DARC 193 film subsequent to O_2 plasma ashing for

1   photoresist removal, as a function of process conditions specified on scale 602. Again, SF

2   represents single frequency plasma deposition of the film, while MF indicates multiple

3   frequency deposition. Ar represents the use of argon as the inert gas in the plasma source

4   gas, while He represents the use of helium. A review of Figure 6 clearly indicates that the

5   extinction coefficient k of the nitrogen-free DARC 193 film experiences less of a

6   reduction after the O_2 ashing when multiple frequency PECVD deposition of the film is

7   carried out, when helium is used as the inert gas in the plasma source gas, and when the

8   film deposition rate is slower. Curve 606 represents the DARC 193 film having an initial

9   extinction coefficient of 0.35; Curve 608 represents the film having an initial extinction

10   coefficient of 0.6, and Curve 610 represents the film having an initial extinction

11   coefficient of 0.95. The slower reduction in extinction coefficient which occurs upon O_2

12   ashing clearly correlates with the increase in compressive strength of the film which is

13   illustrated in Figure 5.

14   [0092]   Figure 7 is a graph 700 which shows the reduction in extinction coefficient on

15   scale 704 for the nitrogen-free DARC 193 film after 9 days of standing a room temperature

16   in a clean room ambient, as a function of process conditions specified on scale 702.

17   Again, SF represents single frequency plasma deposition of the film, while MF indicates

18   multiple frequency deposition. Ar represents the use of argon as the inert gas in the plasma

19   source gas, while He represents the use of helium. Curve 706 represents the DARC 193

20   film having an initial extinction coefficient of 0.35, Curve 708 represents the film having

21   an initial extinction coefficient of 0.6, and Curve 710 represents the film having an initial

22   extinction coefficient of 0.95. A review of Figure 7 clearly indicates that the extinction

23   coefficient k of the nitrogen-free DARC 193 film experiences less of a reduction after

1   standing in the clean room when multiple frequency PECVD deposition of the film is

2   carried out, when helium is used as the inert gas in the plasma source gas, and when the

3   film deposition rate is slower. Although the correlation is not as good as for O_2 ashing,

4   clearly the shelf life of the extinction coefficient for the nitrogen-free DARC 193 film also

5   correlates with the increase in compressive strength of the film which is illustrated in

6   Figure 5.

7   [0093]   Figure 8 is a graph 800 which shows the reduction in refractive index n on

8   scale 802 for the nitrogen-free DARC 193 film as a function of the compressive stress of

9   the film indicated on scale 804. Curve 806 represents the DARC 193 film having an initial

10   extinction coefficient of 0.35, Curve 808 represents the film having an initial extinction

11   coefficient of 0.6, and Curve 810 represents the film having an initial extinction coefficient

12   of 0.95. Figure 8 shows that a nitrogen-free DARC 193 film having a higher compressive

13   strength initially will provide a smaller change in refractive index after O_2 ashing. Figure 8

14   also shows that a nitrogen-free DARC 193 film having a higher extinction coefficient

15   initially (due to atomic composition) is subject to a greater proportional reduction

16   in magnitude after O_2 ashing as the initial compressive stress of the film decreases.

17   [0094]   Figure 9 is a graph 900 which shows the reduction in extinction coefficient k

18   on scale 902 for the nitrogen-free DARC 193 film as a function of the compressive stress

19   of the film indicated on scale 904. Curve 906 represents the DARC 193 film having an

20   initial extinction coefficient of 0.35, Curve 908 represents the film having an initial

21   extinction coefficient of 0.6, and Curve 910 represents the film having an initial extinction

22   coefficient of 0.95. Figure 9 shows that a nitrogen-free DARC 193 film having a higher

29

1   compressive strength initially will provide a smaller change in extinction coefficient after

2   O_2 ashing.

3   [0095]   According to Fourier Transform Infrared Spectroscopy (FTIR) data with

4   respect to the presence of an -OH absorption peak, a nitrogen-free DARC 193 film

5   produced using single frequency PECVD which exhibits a lower compressive stress is

6   more susceptible to moisture absorption.

7   [0096]   No -OH absorption peak was observed for nitrogen-free DARC 193 films

8   produced using multiple frequency PECVD. This suggests that the use of multiple

9   frequency power input during film deposition produces a higher compressive stress film

10   which is resistant to H_2O absorption. As a result, photoresist poisoning will be reduced

11   when DARC 193 films are produced using multiple frequency PECVD.

12   [0097]   Cross-sectional scanning electron microscope images for photoresists

13   patterned to approximately 90 nm feature sizes (in a lines and spaces pattern) have

14   indicated that footing at the bottom of the photoresist after development is substantially

15   reduced when the nitrogen-free DARC 193 film underlies the photoresist, compared with a

16   prior art nitrogen-containing DARC film. The amount of footing is further reduced when

17   multiple frequency PECVD deposition of the DARC 193 film is used rather than single

18   frequency PECVD deposition. Use of helium as the inert gas in the multiple frequency

19   PECVD deposition of the film reduces the footing even more. Finally, the least footing

20   observed when a slower deposition rate for the film is combined with the multiple

21   frequency/helium PECVD deposition.

22   [0098]   The above described exemplary embodiments are not intended to limit the

23   scope of the present invention, as one skilled in the art can, in view of the present

1   disclosure expand such embodiments to correspond with the subject matter of the

2   invention claimed below.